

Evidence for Point Nodes in the Superconducting Gap Function in the Filled Skutterudite Heavy-Fermion Compound $\text{PrOs}_4\text{Sb}_{12}$: ^{123}Sb -NQR Study under Pressure

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(Received February 6, 2008)

We report ^{123}Sb nuclear quadrupole resonance (NQR) measurements of the filled skutterudite heavy-fermion superconductor $\text{PrOs}_4\text{Sb}_{12}$ under high pressures of 1.91 and 2.34 GPa. The temperature dependence of NQR frequency and the spin-lattice relaxation rate $1/T_1$ indicate that the crystal-electric-field splitting Δ_{CEF} between the ground state Γ_1 singlet and the first excited state $\Gamma_4^{(2)}$ triplet decreases with increasing pressure. The $1/T_1$ below $T_c = 1.55$ K at $P = 1.91$ GPa shows a power-law temperature variation and is proportional to T^5 at temperatures considerably below T_c , which indicates the existence of point nodes in the superconducting gap function. The data can be well fitted by the gap model $\Delta(\theta) = \Delta_0 \sin \theta$ with $\Delta_0 = 3.08k_{\text{B}}T_c$. The relation between the superconductivity and the quadrupole fluctuations associated with the $\Gamma_4^{(2)}$ state is discussed.

KEYWORDS: $\text{PrOs}_4\text{Sb}_{12}$, superconductivity, NQR, pressure

The filled skutterudite compound $\text{PrOs}_4\text{Sb}_{12}$ is the first praseodymium (Pr)-based heavy-fermion superconductor with $T_c = 1.85$ K.¹ The heavy-electron mass has been confirmed by the large specific heat jump $\Delta C/T_c \sim 500 \text{ mJ}/(K^2\text{mol})$ at T_c ^{1,2} and by de Haas-van Alphen effect measurements.³ The ground state of the crystal electric field (CEF) for a Pr^{3+} ion is a Γ_1 singlet, which is separated by the first excited state of the $\Gamma_4^{(2)}$ triplet by a gap of $\Delta_{\text{CEF}} \sim 10 \text{ K}$.⁴⁻⁹ Because of this small Δ_{CEF} , the relation between the quadrupole fluctuations associated with the $\Gamma_4^{(2)}$ state^{5,10} and the occurrence of the superconductivity has been the focus of discussions.^{9,11,12}

Although the superconducting gap function is important for understanding the superconductivity in $\text{PrOs}_4\text{Sb}_{12}$, it has not yet been determined experimentally. Previous nuclear-quadrupole-resonance (NQR) measurement has revealed the unconventional nature of the superconductivity.¹³ The spin-lattice relaxation rate $1/T_1$ shows no coherence peak just below T_c , nonetheless, it follows an exponential temperature dependence at low temperatures. On the basis of this result and the exponential decrease in the penetration depth below T_c found by muon spin relaxation (μSR),¹⁴ it has been proposed that the superconducting gap for $\text{PrOs}_4\text{Sb}_{12}$ is isotropic.^{13,14} In contrast, oscillations with respect to the magnetic field angle have been found in angle-resolved thermal conductivity measurements, which suggest that the superconducting gap is anisotropic, and the existence of point nodes in the gap function has been proposed.¹⁵ The results of penetration depth measurement also suggested a point-nodes gap.¹⁶ Our previous NQR study on the substitution system $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$ strongly suggested the existence of nodes in the superconducting gap function of $\text{PrOs}_4\text{Sb}_{12}$, since Ru doping at the Os site in $\text{PrOs}_4\text{Sb}_{12}$ as a nonmagnetic impurity induces a

residual density of states in the superconducting gap,¹⁷ but the nodal structure remains unclear.

In this paper, we report on the ^{123}Sb -NQR study of $\text{PrOs}_4\text{Sb}_{12}$ under pressure. Applying pressure reduces T_c ² and may also change Δ_{CEF} ,¹⁸ and therefore can provide new information on the symmetry of the superconducting gap as well as on the mechanism of the superconductivity. We find that Δ_{CEF} decreases with increasing pressure, and that at $P = 1.91$ GPa, $1/T_1$ decreases in proportion to T^5 at low temperatures, which indicates point nodes in the superconducting gap function.

Single crystals of $\text{PrOs}_4\text{Sb}_{12}$ were grown by the Sb-flux method. For NQR measurements, the single crystals were powdered to allow the rf magnetic field to penetrate into the sample. However, the size of the grains is kept larger than $100 \mu\text{m}$ to avoid crystal distortions. Hydrostatic pressure was applied using a NiCrAl/BeCu piston-cylinder cell, filled with Si oil as a pressure-transmitting medium.¹⁹ The pressure at low temperatures was determined from the pressure dependence of the T_c value of Sn metal measured by a conventional four-terminal method. Data below 1.4 K were collected using a $^3\text{He}/^4\text{He}$ dilution refrigerator at $P = 0$ and a ^3He refrigerator under high pressure $P = 1.91$ GPa. To avoid possible heating due to the rf pulses, we used very small amplitude rf pulses in the T_1 measurements at low temperatures. We confirmed the lack of such a heating effect by ensuring that the spin echo intensity is not affected by an rf pulse with a slightly off-resonance frequency, which was applied before the $\pi/2 - \pi$ pulse sequence.

The Sb nuclei have two isotopes of ^{121}Sb and ^{123}Sb with natural abundances of 57.3% and 42.7%, respectively. Since ^{121}Sb and ^{123}Sb have the nuclear spins $I = 5/2$ and $7/2$, respectively, five Sb-NQR transitions are observed.¹³ In the present experiment, all measure-

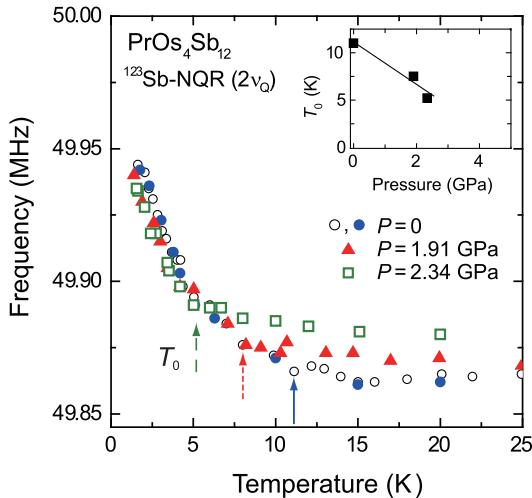


Fig. 1. (color online) Temperature dependence of $2\nu_Q$ position of ^{123}Sb -NQR ($\pm 3/2 \leftrightarrow \pm 5/2$ transition) at $P = 0$ (solid circles), 1.91 (solid triangles), and 2.34 GPa (open squares) along with the data at $P = 0$ (open circles) by Kotegawa *et al.*¹³ Solid, dotted, and dashed arrows indicate T_0 at $P = 0$, 1.91, and 2.34 GPa, respectively (see text). The inset shows the pressure dependence of T_0 .

ments were carried out at the $\pm 3/2 \leftrightarrow \pm 5/2$ transition (hereafter, $2\nu_Q$ transition for short) of the ^{123}Sb nucleus. Figure 1 shows the increase in the $2\nu_Q$ resonance frequency below $T = 25$ K for various pressures. T_0 is the temperature at which the $2\nu_Q$ resonance frequency increases abruptly. Since the electrical field gradient (EFG) is predominantly determined by the on-site charge distribution, the NQR frequency is a good measure of the population of the ground/excited state. Indeed, in both $\text{PrOs}_4\text{Sb}_{12}$ ¹³ and $\text{PrRu}_4\text{Sb}_{12}$,²⁰ T_0 is in good agreement with Δ_{CEF}/k_B . More recently, it has been suggested that the temperature dependence of NQR frequency can be accounted for by the EFG associated with the hexadecapole moment of the $\Gamma_4^{(2)}$ state.²¹ Therefore, the increase in the NQR frequency below T_0 indicates that the depopulation of the $\Gamma_4^{(2)}$ state occurs below this temperature. As seen in Fig. 1, T_0 shifts to lower temperatures $T_0(P) \sim 7.5$ and 5 K at $P = 1.91$ and 2.34 GPa, respectively (also see Fig. 1 inset). These results provide evidence that Δ_{CEF} decreases with increasing pressure.

The above conclusion is supported by the pressure effect on the temperature dependence of $1/T_1T$. Figure 2 shows the temperature dependence of $1/T_1T$ at $P = 0$ and 1.91 GPa. The pressure effect appears below 4 K. At $P = 0$, the reduction of $1/T_1T$ results in a peak in the plot of $1/T_1T$ versus T , which is due to the depopulation of the $\Gamma_4^{(2)}$ state below T_0 . At $P = 1.91$ GPa, the decrease in $1/T_1T$ occurs at a lower temperature, indicating the decrease in Δ_{CEF} . These results are consistent with the conclusion inferred from the magnetization measurement.¹⁸

We find concomitantly that the temperature of the onset of the superconducting transition decreased with increasing pressure, in agreement with previous reports.^{2,18} The inset in Fig. 3 shows the temperature de-

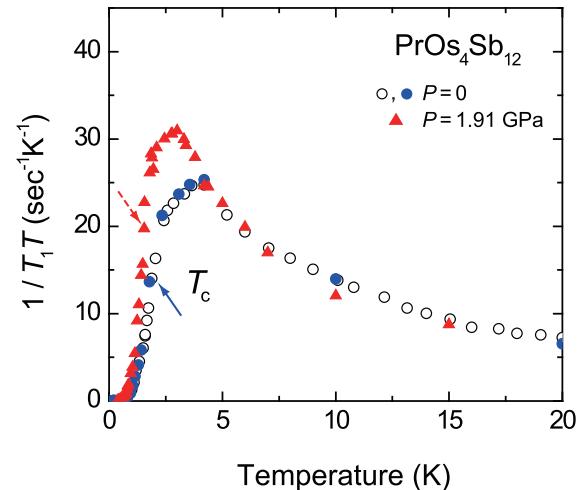


Fig. 2. (color online) Temperature dependence of $1/T_1T$ at $P = 0$ (solid circles) and 1.91 GPa (solid triangles) along with the data at ambient P cited from literature¹³ (open circles). Solid and dotted arrows indicate $T_c(P)$ at $P = 0$ and 1.91 GPa, respectively.

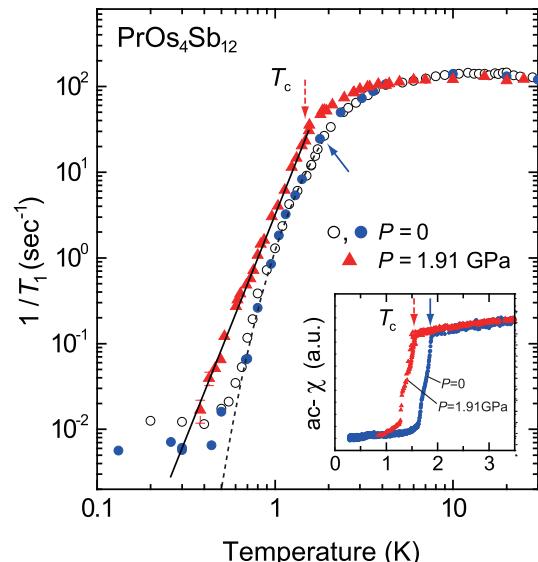


Fig. 3. (color online) Temperature dependence of $1/T_1$ at $P = 0$ (solid circles) and 1.91 GPa (solid triangles) along with the data at ambient P cited from ref. 13 (open circles). The straight line is a guide to the eyes. The dotted curve depicts the relation $1/T_1 \propto \exp(-\Delta_0/k_B T)$ with $\Delta_0/k_B T_c = 3.45$, proposed by Yogi *et al.*²³ The inset shows the temperature dependence of ac-susceptibility at $P = 0$ and 1.91 GPa. Solid and dotted arrows indicate T_c at $P = 0$ and 1.91 GPa, respectively.

pendence of ac-susceptibility measured using the NQR coil. T_c decreased from 1.85 K at $P = 0$ to 1.55 K at $P = 1.91$ GPa. The main panel of Fig. 3 shows the temperature dependence of $1/T_1$ at $P = 0$ and 1.91 GPa. The ambient-pressure data are in excellent agreement with those reported previously (open circles),¹³ except that $1/T_1$ below $T \sim 0.4$ K is smaller in the present sample, probably due to the improvement of the sample quality.²² The data could be fitted by an exponential function $1/T_1 \propto \exp(-\Delta_0/k_B T)$ below T_c , as pointed out previously.¹³ At both $P = 0$ and 1.91 GPa, $1/T_1$ is T -

independent above T_0 , indicating that the relaxation in the high-temperature region is predominated by the Pr- $4f^2$ -derived localized magnetic moments. With decreasing temperature below T_0 , $1/T_1$ starts to decrease. Below T_c , no coherence peak is observed at $T_c = 1.55$ K for $P = 1.91$ GPa, as for $P = 0$.¹³ However, the T dependence of $1/T_1$ at high pressure is markedly different from that at ambient pressure. $1/T_1$ at $P = 1.91$ GPa decreases in a power law of T below T_c .

In particular, below $T \sim 0.55$ K, $1/T_1$ is proportional to T^5 , as can be seen more clearly in Fig. 4. We find that a point-nodes model, with a low-energy (E) superconducting density of states (DOS) proportional to E^2 , can well explain the experimental result. In Fig. 4, the curve below T_c is a fit to the Anderson-Brinkman-Morel (ABM) model.^{24,25} Namely,

$$\frac{T_1(T_c)}{T_1} = \frac{2}{k_B T} \int \left(\frac{N_S(E)}{N_0} \right)^2 f(E)[1 - f(E)] dE,$$

where $N_S(E)/N_0 = E/\sqrt{E^2 - \Delta^2}$ with $\Delta(\theta) = \Delta_0 \sin \theta$. The fit gives $\Delta_0/k_B T_c = 3.08$. The penetration depth data at ambient pressure seem to be consistent with our results.¹⁶ However, the $p + h$ models²⁶ proposed to explain the thermal conductivity would give a T^3 -like dependence, since the DOS at low- E is linear in E , and is therefore not compatible with our data.

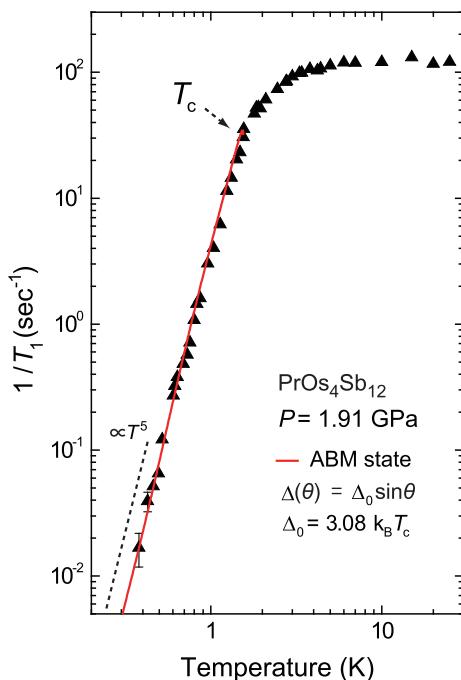


Fig. 4. (color online) Temperature dependence of $1/T_1$ at $P = 1.91$ GPa. The arrow indicates T_c . The solid curve is a fit assuming the ABM state with $\Delta_0/k_B T_c = 3.08$. The dotted line indicates the relation of $1/T_1 \propto T^5$ considerably below T_c .

It has been proposed that the superconductivity is mediated by the excitons due to the $\Gamma_4^{(2)} - \Gamma_1$ quasi-quartet.¹¹ In such case, T_c would increase when Δ_{CEF}

is reduced. Clearly, our results do not lend a straightforward support to this theory. Further experimental study under higher pressure is highly desirable. Finally, we comment on the different temperature dependences of $1/T_1$ at $P = 0$ and 1.91 GPa. Two possible causes could be responsible. First, the larger gap Δ_{CEF} may contribute to the reduction of $1/T_1$ below T_c at ambient pressure, which makes the temperature dependence of $1/T_1$ exponential.²⁷ Recent thermal conductivity measurement under a magnetic field suggests the superconductivity at ambient pressure is induced in two different Fermi sheets,²⁷ which may have different symmetry. The sheet in which nodes develop may grow significantly under high pressures.

In conclusion, we have presented the ^{123}Sb -NQR results on the filled skutterudite heavy-fermion compound $\text{PrOs}_4\text{Sb}_{12}$ at $P = 0$, 1.91, and 2.34 GPa. The temperature dependence of NQR frequency and the spin-lattice relaxation rate $1/T_1$ indicate that the gap Δ_{CEF} between the ground state Γ_1 singlet and the first excited state $\Gamma_4^{(2)}$ triplet decreases with increasing pressure. At $P = 1.91$ GPa, the temperature dependence of $1/T_1$ below T_c is well explained by the ABM superconducting state, with point nodes in the gap function. To confirm the mechanism showing why T_c decreases with increasing pressure in $\text{PrOs}_4\text{Sb}_{12}$, further NQR measurements under pressure are now in progress.

We thank K. Matano for his experimental help, and R. Shiina, H. Harima, Y. Kitaoka, H. Tou, M. Ichioka, N. Nakai, H. Kotegawa, and M. Yogi for discussions and comments. This work was supported in part by grants for scientific research, and a grant for Attractive Education in Graduate School "Training Program for Pioneers of Frontier and Fundamental Sciences", from the Ministry of Education, Culture, Sports, Science and Technology.

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